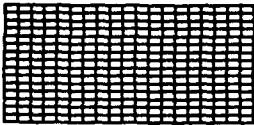


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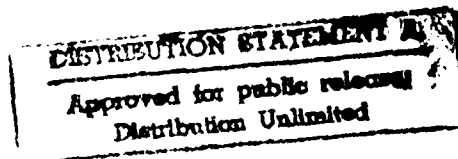
**FABRICATION OF PIEZOELECTRIC  
CERAMIC/POLYMER COMPOSITES BY  
INJECTION MOLDING**

**Final Report: April 15, 1993**

Contract Number N00014-92-C-0010

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Contractor: Materials Systems Inc., Concord, Massachusetts.



Submitted to the Office of Naval Research, Arlington, Virginia  
in fulfillment of contract requirements.

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# FABRICATION OF PIEZOELECTRIC CERAMIC/POLYMER COMPOSITES BY INJECTION MOLDING

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## **FABRICATION OF PIEZOELECTRIC CERAMIC/POLYMER COMPOSITES BY INJECTION MOLDING**

### **Executive Summary**

Piezoelectric ceramic/polymer composites have many applications in advanced Navy transducers and commercial ultrasonic imaging. Unfortunately, their application has been limited by the lack of a manufacturing-viable technology capable of meeting both the low cost and high volume production requirements. The principal manufacturing difficulty lies in the handling of millions of fine PZT fibers during their assembly into a typical composite transducer installation.

In this program, Materials Systems Inc. (MSI) has demonstrated that ceramic injection molding is capable of meeting the stringent transducer cost and assembly needs of piezoelectric ceramic/polymer composites for Navy applications. The injection molding approach overcomes the difficulty of assembling oriented ceramic fibers into composite transducers by net-shape preforming ceramic fiber arrays. Aside from this advantage, the process makes feasible the construction of composite transducers having more complex ceramic element geometries than those previously envisioned, leading to greater design flexibility for improved acoustic impedance matching, lateral mode cancellation and superior actuator performance.

A process development and transducer fabrication effort has been successfully completed to demonstrate the cost-effectiveness and viability of this process for 1-3 composite fabrication. The process has been shown to be capable of forming fine PZT element dimensions ( $<0.5\text{mm}$  diameter) in large quantities, with excellent potential for meeting the scale up and cost goals. A pilot scale production facility has been established and equipped to meet near-term Navy prototype manufacturing needs for these types of composite transducer.

## 1. Objectives and Deliverables.

The objective of this research program was to determine the feasibility of making large-area, fine-scale piezoelectric ceramic/polymer composites at low cost by means of injection molding.

Two types of transducers were planned as the hardware deliverables, viz:

### *Baseline Transducer.*

Materials: Ceramic fibers - PZT-5H.  
Polymer matrix - Spurr epoxy resin.

PZT volume fraction: 12%.

Fiber dimensions (nominal): 0.5 to 1mm diameter (depending on the outcome of transducer fabrication trials and the cost of tooling).

Dimensions: 50mm X 50mm X 6.35mm thick.

### *Transducer Array.*

Materials: Ceramic fibers - PZT-5H.  
Polymer matrix - Spurr epoxy resin.

PZT volume fraction: 12%.

Fiber dimensions (nominal): 0.5 to 1mm diameter.

Dimensions: 200mm X 200mm X 6.35mm thick.

At the request of ONR, minor modifications were made to these deliverables to allow the MSI composites to conform to new design parameters established by ONR during the course of the program. The principal modifications were to increase the PZT volume fraction to 15 percent and to increase the fiber diameter to 1.15mm (i.e. 1mm<sup>2</sup> cross-sectional area).

The program plan for meeting these objectives was as shown in Figure 1.

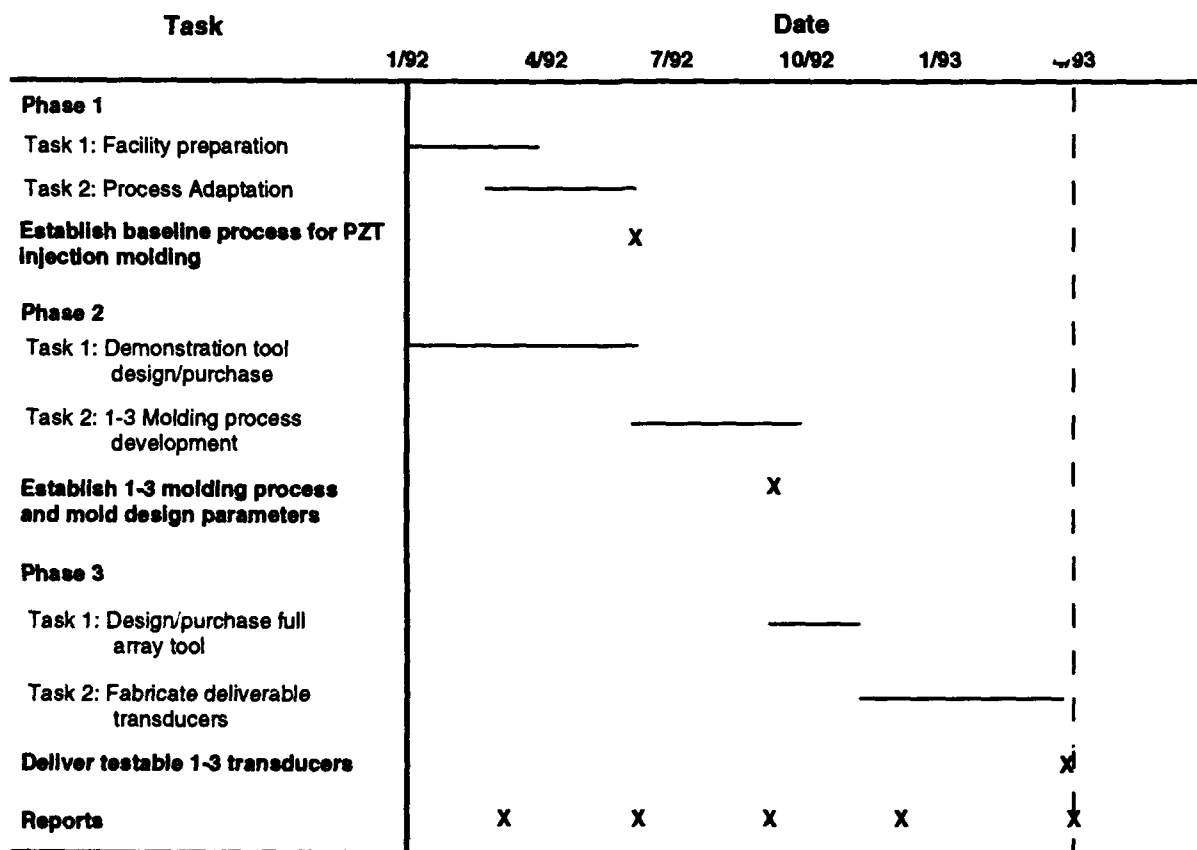


Figure 1. Program Plan

## **2. Accomplishments versus Objectives**

All of the planned objectives were met on schedule and within budget. An injection molding process was developed and then demonstrated by making the specified 1-3 piezoelectric ceramic/polymer composite test pieces for Navy evaluation. The key features of the process include:

- low cost by forming and handling many PZT fibers simultaneously,
- versatility in terms of ceramic element geometry and size,
- high quality ceramic material having excellent piezoelectric properties,
- high process yield,
- rapid throughput,
- scalability, and
- flexibility in the selection of final composite assembly procedure.

Additional work, outside the scope of the original plan but included by MSI to enhance its overall composite fabrication technology and capabilities, was completed as follows:

- The PZT molding process was successfully demonstrated to be capable of forming 0.5mm diameter fiber arrays having an aspect ratio in excess of 16.
- The sintering process was scaled up to be capable of producing 400cm<sup>2</sup> of preform/crucible/day, the pacing process step at this time.
- 50mm square composite demonstration pieces were made having voided polyurethane matrix and bonded face plates as a demonstration of the fabrication viability of the ONR 2m x 2m design.

### 3. Technical Approach

The original 1-3 piezoelectric ceramic/polymer composites\* were fabricated by hand-aligning extruded PZT ceramic rods in a jig and encapsulating in epoxy resin, followed by slicing to the appropriate thickness and poling the ceramic. Aside from demonstrating the performance advantages of this material, this work highlighted the difficulties involved in fabricating 1-3 composites on a large scale, or even for prototype purposes. These are:

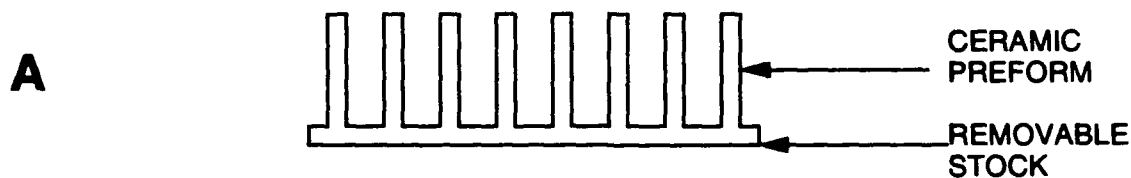
- 1) The requirement to align and support large numbers of PZT fibers during encapsulation by the polymer.
- 2) The high incidence of dielectric breakdown during poling arising from the significant probability of encountering one or more defective fibers in a typical large array.

Both of these difficulties can be resolved by using a net-shape forming method to fabricate the PZT elements as a single-piece array instead of as individual fibers. Such an array is illustrated schematically in Figure 2a. In this configuration, the alignment and spacing of the PZT fibers is maintained using an integral PZT base plate. The MSI technical approach uses injection molding to fabricate such PZT ceramic fiber preforms prior to assembly into composites.

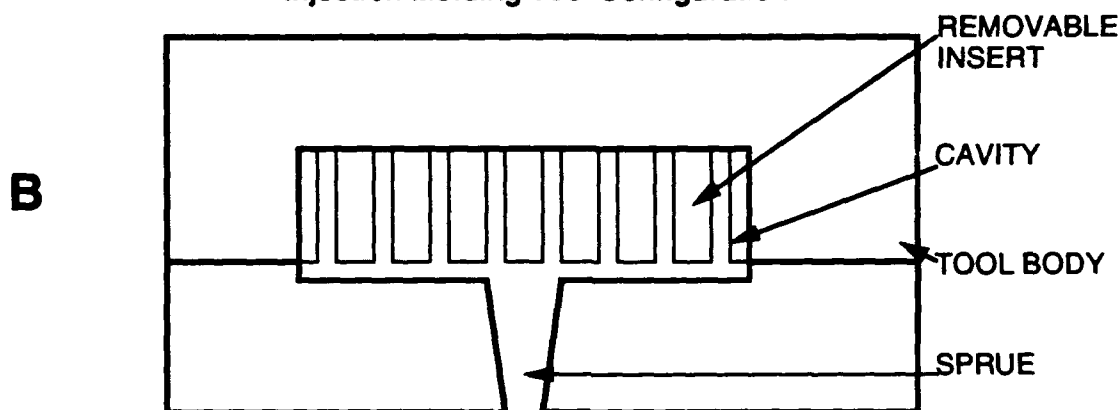
Injection molding is widely used in the plastics industry as a means for rapid mass production of complex shapes at low cost. By injecting a hot thermoplastic mixture of ceramic powder and wax-based binder into a cooled mold, complex ceramic shapes can be formed with the ease and rapidity normally associated with plastics molding. The binder must be removed nondestructively, necessitating high solids loading and careful control of the binder removal process and fixturing. Once the binder is removed, the subsequent firing and poling processes are similar to those used for conventional PZT ceramics.

\* R. Newnham, L. Bowen, K. Klicker and L. Cross, "Composite Piezoelectric Transducers," *Materials in Engineering*, Vol. 2, pp. 93-106, Dec. 1980.

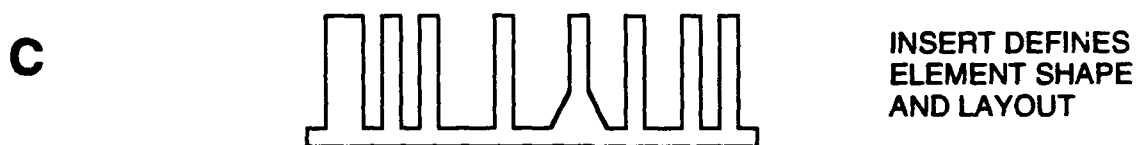
**Preform Configuration (Approx. 400 ceramic elements)**



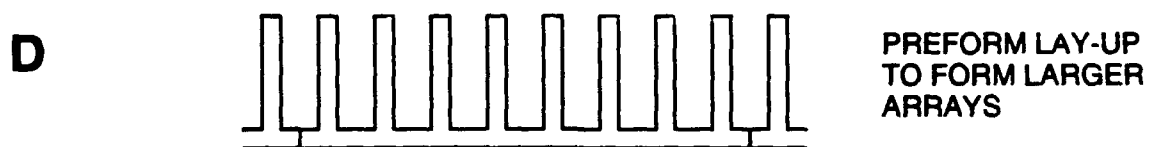
**Injection Molding Tool Configuration**



**Tool Insert Design Permits Composite Design Flexibility**



**Large Area Composite Arrays made from Preforms**



**Figure 2: Composite Fabrication Approach using Injection Molded PZT Preforms.**

The injection molding process offers the following advantages over alternative fabrication routes:

- Complex, near net-shape capability for handling many fibers simultaneously.
- Rapid throughput (typically seconds per part).
- Compatibility with statistical process control.
- Low material waste.
- Flexibility with respect to transducer design  
(allows variation in PZT element spacing and shape).
- Low cost in moderate to high volumes.

Figure 2b illustrates the tooling used to mold a typical PZT ceramic preform. In this approach, shaped tool inserts allow changes in part design without incurring excessive retooling costs. Examples of alternative design configurations are shown in Figure 2c, illustrating possible variations in PZT element geometry and spacing which allow lateral mode cancellation and improve thickness mode acoustic impedance matching. These have not been explored in the current program, but appear entirely feasible using the MSI process. Figure 2d shows how individual preforms can be configured to form larger arrays.

The injection molding process developed for composite preform fabrication is shown schematically in Figure 3. PZT preform fabrication begins with qualification and conditioning of the as-received powder to adjust its properties so that the compounded mix rheology falls within an acceptable molding range. The powder conditioning process can accommodate a wide range of powders, thus allowing the Navy to substitute other PZT or PMN formulations having different piezoelectric properties when needed. The powder is homogeneously mixed with a wax-based binder and molded using a hard-faced screw-type injection molder to form the green PZT preform shape. Dewaxing is accomplished by slowly heating the molded parts in air until all organic materials have been removed. The parts can then be sintered in closed crucibles, encapsulated in the selected polymer matrix, ground flat and parallel, and poled prior to testing.

The technical approach has addressed process refinement and transducer fabrication in three distinct phases. In the first phase, a pilot-scale production facility was set up for PZT molding, and the existing generic ceramic injection

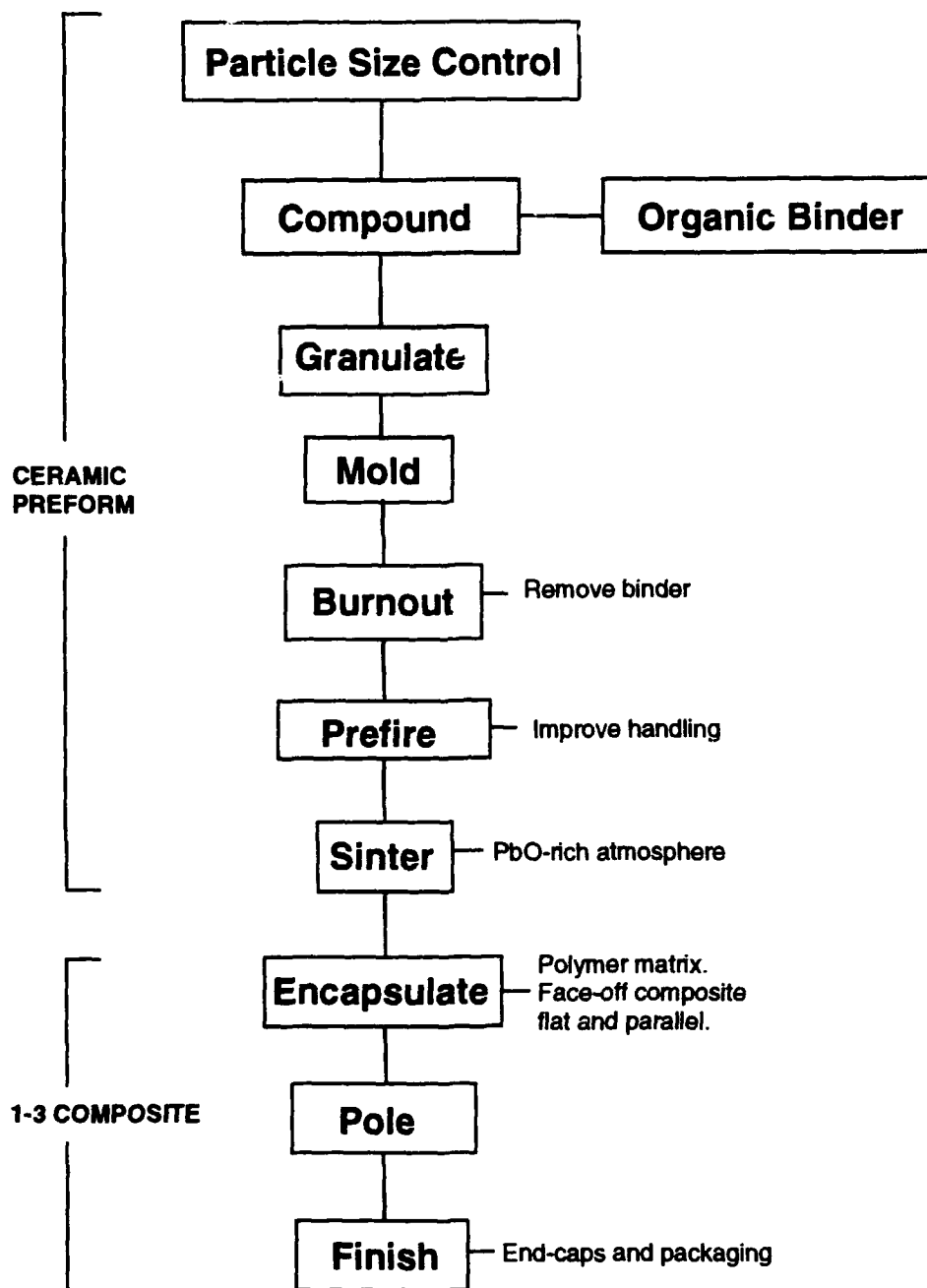
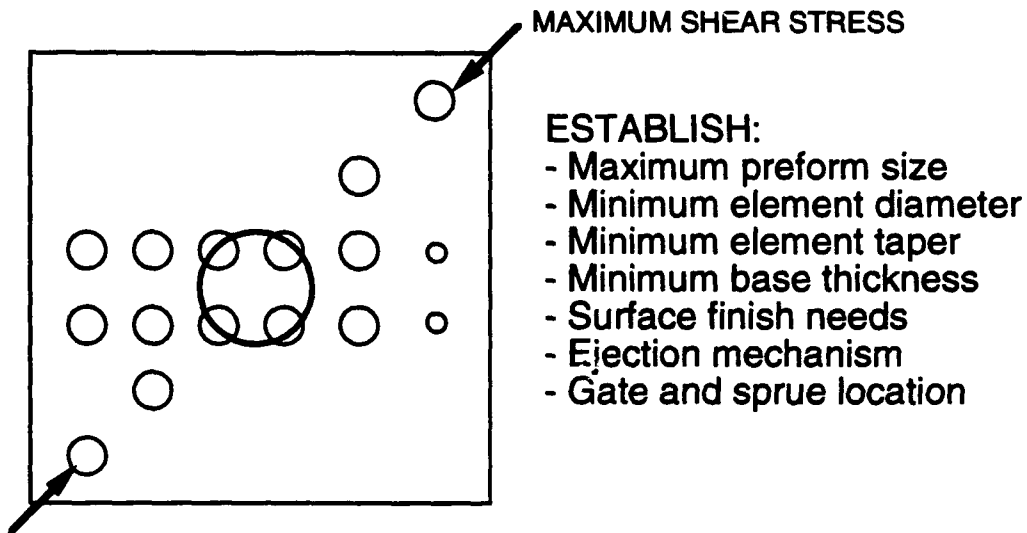


Figure 3: Composite fabrication route.

molding process adapted to accommodate specific PZT molding requirements. The process was then demonstrated on simple cross-section parts.

In the second phase, molding experiments were conducted in tooling specially designed to simulate full-scale baseline transducer fabrication. This step was necessary to establish the limits of the process in terms of mold design without incurring the extra cost of fabricating several different tools, each having a full array of PZT elements, to test each possible tool configuration. In particular, this tool has allowed a determination of the effects of mold cooling-induced shear stress on part integrity, the optimum gating configuration, and the surface finish requirements for intact part removal. In the third phase, tooling was designed and purchased for fabrication of testable transducers and the process and tooling refinements were brought together to meet program parts deliverables. Figure 4 shows schematically the layout of the demonstration tool used for tool design verification purposes and the full array tool used for transducer fabrication.

### A. TEST CONFIGURATION



### B. FINAL CONFIGURATION

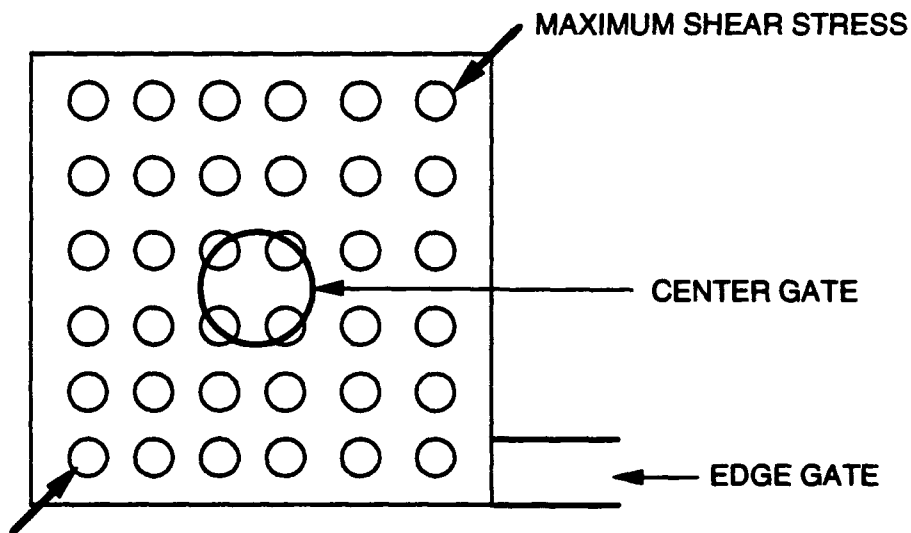


Figure 4: Demonstration tool layout - schematic.

## 4. Results

As part of this program, Materials Systems set up a dedicated facility equipped for injection molding PZT composite preforms and assembling finished composites. For this purpose MSI purchased the full range of process equipment needed for ceramic preform fabrication and composite processing. Although it was originally estimated that facility set-up would take approximately three months to reach full operation, the task was actually accomplished in two months.

For convenience of presentation, the results of this program have been divided into two separate sections. One is devoted to ceramics process development and the ceramic preform fabrication issues, while the other deals with composite fabrication and testing.

### 4.1 Ceramic Preform Fabrication

Figure 5 shows the process steps involved in fabricating 1-3 PZT ceramic preforms. Technical issues associated with the development of each process step are discussed individually below. It is important to note that the process steps are highly interactive. Resolving difficulties with the later process procedures, such as binder removal and sintering, has required a detailed understanding of these process interactions. The technical approach was designed to elucidate the best conditions as well as the process interactions so that variations in one process step have minimal impact on overall yield and product quality.

#### *Powder Process Development*

The PZT powder utilized for this contract was a soft PZT-5H formulation, specified by ONR and purchased from Morgan Matroc Vernitron Division, Bedford, Ohio. Table 1 shows manufacturer-measured data for pressed and sintered samples from this powder (lot 105A).

The first step in implementing the MSI process for PZT was to establish basic milling conditions for the powder to allow preparation of PZT/binder formulations which fall within acceptable molding and burn-out process parameter ranges. Prior to milling, it was found necessary to perform a low temperature calcine on

**Table 1: Properties of Pressed and Sintered Samples from Lot 105A**

<u>Property</u>	<u>PZT-5H (105A)</u>
K33 T	3584
DF	0.0180
QM	66
density	7.51
kp	0.6567
k31	0.3857
d33	744.8
d31	282.7
g33	23.47
g31	8.91
Np	1925
sE11	16.93
sD11	14.41
YE11	5.906
YD11	6.938

the as-received PZT-5H powder to remove organic dispersants incorporated by the manufacturer. Milling was performed in polymer-lined containers using aged zirconia media to minimize contamination. No evidence of contamination from milling was found in any of the subsequent work.

To optimize the milling process, a parametric milling study was performed in which the effects of various milling conditions were characterized by conducting compounding trials with the wax binder. For this purpose, the PZT volume fraction was set at levels representative of injection molding and the compounding was performed under controlled shear rate conditions. The compounded materials were then characterized by torque and melt-index rheometry and by actual molding trials on simple cross-section parts. Using this approach, a set of milling conditions was established which facilitated control of the green ceramic process. For larger volumes of material, alternative milling methods have been identified to accelerate this process step and improve throughput.

### *Compounding*

Based on the results of milling process development, a limited study of compounding behavior at two solids loadings and several shear rates was completed. The resulting PZT powder/binder mixtures were characterized using melt index rheometry and found to have sufficiently low viscosity to attempt molding trials. For this purpose, compounding was scaled up directly to 4kg batches to allow full operation of the molding equipment. This scale up was successful over a wide range of solids loadings, provided the mix viscosity was kept sufficiently low to prevent equipment abrasion and mix contamination.

Experience has shown that an ultimate test of the compounding process efficacy must include sequential molding, burnout and sintering trials conducted on representative simple cross-section parts. Existing tooling was used to mold simple demonstration pieces (modulus of rupture test bars) and then conduct binder burnout and sintering studies. The test specimens were characterized by optical microscopy and bulk density measurements to monitor product quality in terms of process parameter variations, and the green process/sintered density relationships were measured to establish shrinkage factors for 1-3 preform tool design.

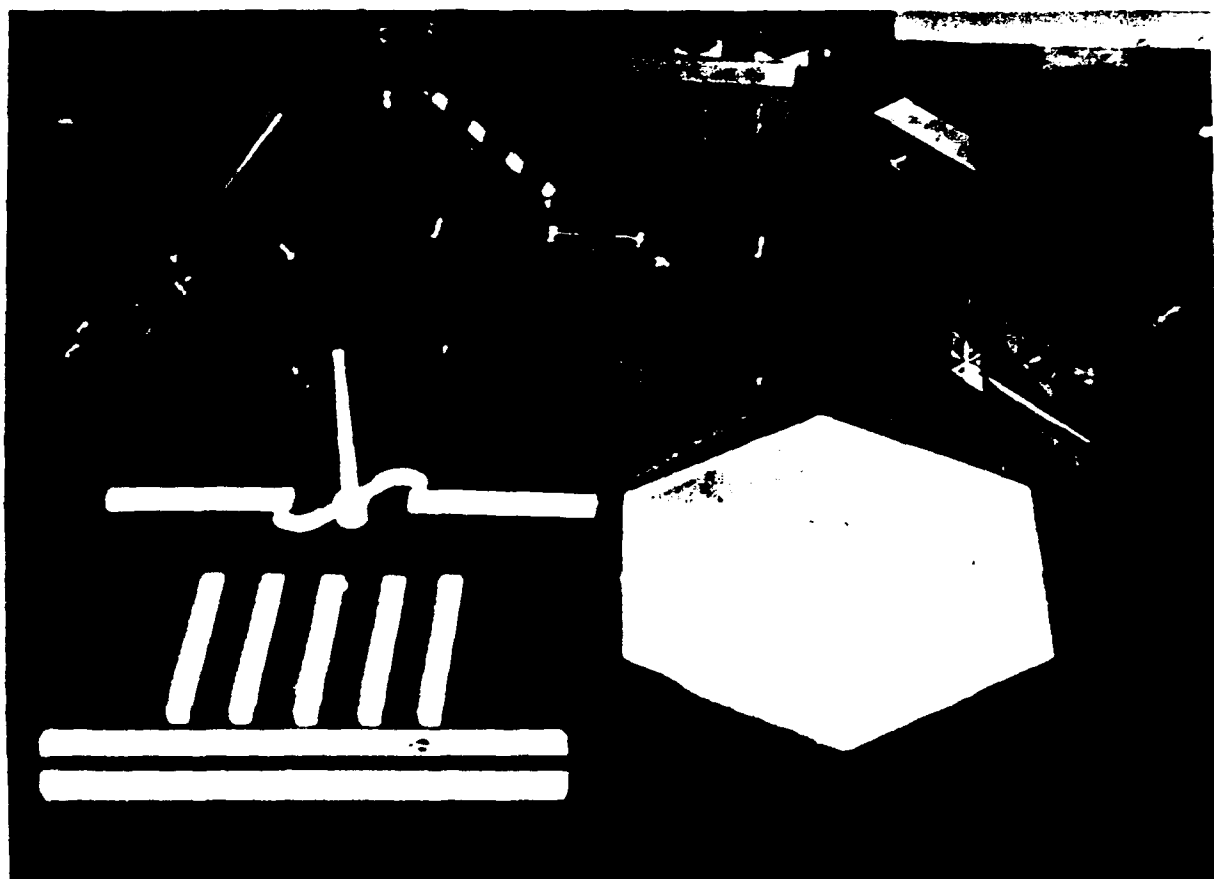


Figure 5: Injection molding tool used for simple PZT bar shapes.

The overall result of the compounding experiments was a determination that the powder/binder ratio could be varied over a wide range (up to 10 volume percent) and still made to work in molding. However, the highest yields of acceptable parts fell within a narrower process window of about 2 volume percent. This powder/binder ratio range has proved sufficient for fine-tuning the green density to allow for powder batch variations and accurate dimensional control in the sintered parts.

### *Molding*

Molding process development was accomplished in parallel with tool design and fabrication, iterating both activities together to achieve the desired results. The best molding conditions were determined using established experimental approaches involving complete process cycles, including binder removal and sintering. The following process parameters were expected to be important and were therefore emphasized:

- a) Cavity filling (solids loading, gate location and geometry, mold temperature and temperature distribution, peak cycle pressure, mold vacuum, element diameter).
- b) Part removal (release agent, element taper and dimensions, tool surface finish, removal temperature, forced removal, shear forces on outer elements due to thermal contraction in the tool).

Molded part ejection was expected to present a technical challenge since the mold insert required almost 400 individual cavities and the molding binder had limited mechanical strength. Consequently, an appropriate ejection mechanism was designed to consistently enable freshly-molded parts to be removed intact with minimal residual stress. As part of the tooling design phase, tooling options were explored with two vendors, both familiar with the MSI process, to ensure that the most viable ejection approaches were considered.

One vendor proposed a conventional plastics ejection design while the other offered an additional design geared towards accommodating the properties of the MSI molding binder. Conventional plastics injection molding ejection was

considered questionable for this application because of a tendency for the wax-based binder to distort under high pressure after freezing. However, in order to minimize technical uncertainties, MSI decided to evaluate both vendors' approaches by designing a demonstration mold (Figure 4) with cavities operated using both ejection mechanisms. Allowing for technical differences in the vendor's proposals, the cost of both approaches was similar. Consequently, a purchase order was placed with the vendor offering both ejection routes to manufacture the tool. In addition to the two ejection mechanisms, this tool contained fiber cavities having three different surface finishes, two 0.5mm diameter fibers as well as 1mm fibers having three different draft angles (0,1 and 2 degrees), cavities in the diametrically-opposed corners to evaluate cooling-induced shear effects, and three different preform base thicknesses to evaluate cavity filling.

While the demonstration tool was in preparation, a simple bar-shaped tool insert was designed and fabricated to perform mold filling experiments. For this purpose, an existing injection molding tool insert (Figure 5) was modified to incorporate several cavities having dimensions similar to those in the demonstration tool (see Figure 6). Molding trials using this modified tool provided early information on the efficacy of cavity filling for mold design purposes. These experiments showed that cavity filling was straightforward, even into 1mm diameter blind holes having no air venting. Removing the molded parts from the cavities proved very difficult since no ejection mechanism was incorporated into this simple insert. The molded parts revealed surface blemishes which indicated defects in the EDM-formed holes. This information was fed back to the mold maker for use in building the full array injection molding tool.

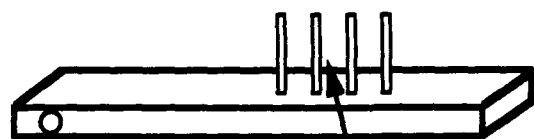
Other molding trials were performed using simple cross-section 50x6x3mm bars to establish the effects of molding parameters, such as pressure, temperature and solids content on part quality. In addition, these trials produced approximately 150 bars for use in binder burn-out and sintering studies.

The demonstration tool was completed by the outside vendor and received by MSI on 5/27/92. The tool was set up for molding and used for the first trials without any attempt to optimize molding conditions. The cavity filled completely without flashing, indicating a high quality tool. Both of the ejection mechanisms described earlier were effective in pushing out the as-molded PZT fibers, even though the

## PZT Bar Configuration



## Modified PZT Bars



Simulated Insert Cavity  
(no forced ejection)

Figure 6: Bar tool modified to simulate fiber cavities.

surface finish of the individual cavities exhibited EDM marks. This preliminary tool shake-down showed that two modifications were required: Firstly, an improved surface finish in the cavities, and secondly a modification to the ejection mechanism to improve part release over all surfaces of the molded fibers. After these changes were made by the tool vendor, it became possible to eject parts intact.

Figures 7 and 8 illustrate the surfaces of as-molded and as-sintered fibers, showing the presence of shallow fold lines approximately  $10\mu\text{m}$  wide, which are characteristic of the injection molding process. The fibers exhibit minor grooving along their length due to ejection from the tool. Controlling the packing behavior and therefore the incidence of fold line formation has been accomplished by adjustment of the key molding parameters (tool and barrel temperature and injection pressure), as well as the feedstock rheology. On the as-fired surface of the fibers the fold lines are extremely shallow, ( $\sim$ one grain diameter deep), and the grain size range is typical of fired PZT at  $2\text{-}5\mu\text{m}$  diameter.

Using the demonstration tool and molding process conditions established using the simple bar tool (Figure 5), all of the process steps were examined experimentally to determine those conditions which produced the highest quality 1-3 composite preforms. Early molding trials showed that shrinkage during cooling from the molding temperature did not cause damage to the outermost PZT elements. Consequently, the size of the tool cavity was set at  $50\text{mm} \times 50\text{mm}$ , for a fiber count of 361 per full-array preform. All of the fiber cavities filled during molding; surprisingly, the fill pattern improved when the PZT base thickness was reduced to the lowest available level of  $1.5\text{mm}$ . Both ejection mechanisms succeeded in removing the molded parts; however, the conventional plastics type was abandoned because it proved complex and unreliable, and was limited to PZT elements larger than  $0.75\text{mm}$  diameter.

Following this decision the tool inserts were returned to the manufacturer for polishing and to have the corner diagonal cavities welded closed. Figure 9 shows an injection molded part made with the modified cavity. The process was shown to be capable of forming green fibers  $0.5\text{mm}$  diameter by  $9\text{mm}$  long, and to require less than one degree taper angle along the fiber length for successful ejection.

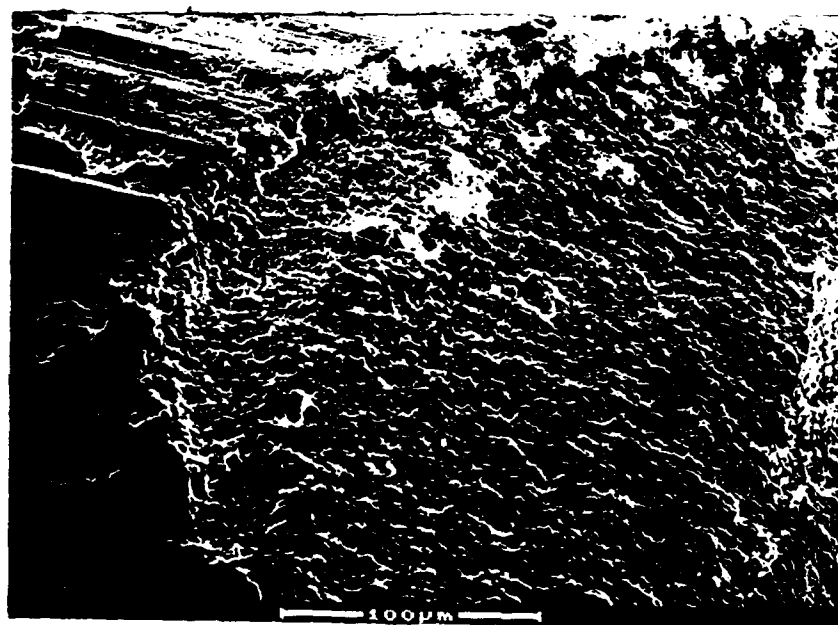
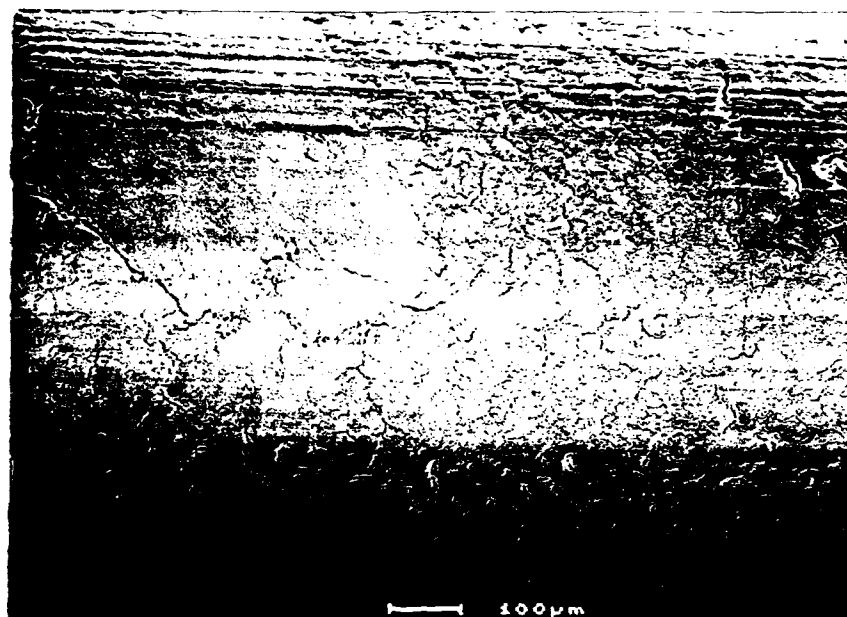


Figure 7: Scanning electron micrograph of as-molded surface of PZT fiber, showing shallow fold lines formed during packing into the mold cavity and void-free interior of the fiber.



Figure 8: Scanning electron micrograph of as-sintered surface of PZT fiber, showing the PZT grain size.

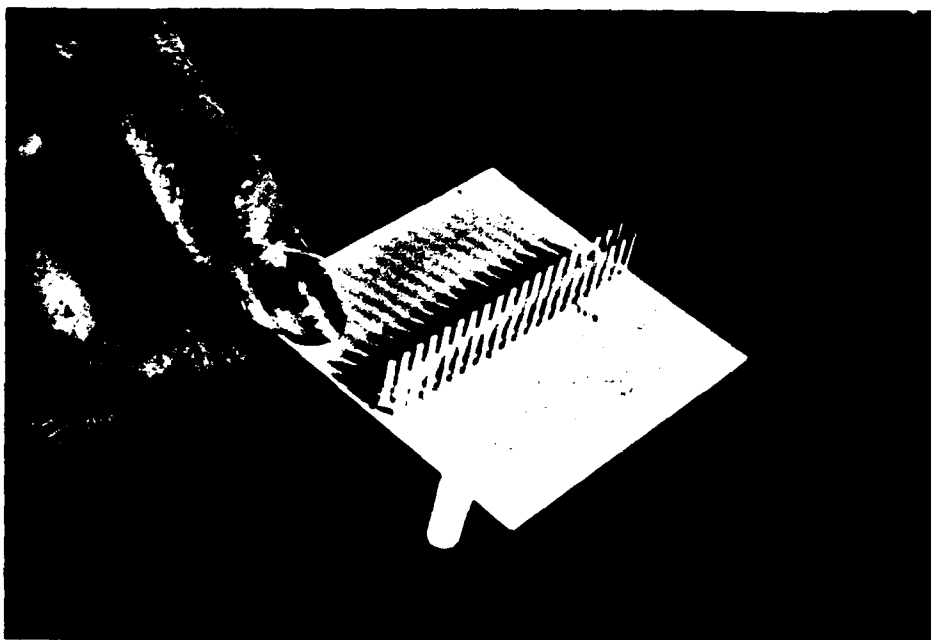


Figure 9: Injection molded PZT part made using the demonstration tool.

To further explore the limits of the process in terms of PZT fiber diameter and aspect ratio, a new set of inserts was fabricated having two parallel rows of fibers only 0.5mm diameter with 0.5 degree taper angle. This insert was successfully employed to form 0.5mm diameter PZT fiber preforms having an aspect ratio of 16, compared with approximately 5 required by the current ONR 1-3 composite design specification. Figure 10 shows molded and sintered demonstration preforms made using the 0.5mm diameter cavity tool.

In all, the demonstration tool inserts were reworked four times as part of the learning process required to design a properly functioning full array tool. Specifications were set for cavity surface finish, taper angle, fiber length and diameter, ejection mechanism, gating, steel hardness, bearing surface area, insert sliding tolerances and ease of disassembly for servicing.

For the full array tool, the fiber diameter was set at 1.12mm and the fiber length at 8mm, with a taper angle of 0.5 degrees. These dimensions correspond to a PZT content of 15 volume percent in the 1-3 composite, the value selected by ONR at the 8/25/92 ONR program review for the fabrication of a 2m x 2m array. An order was placed for the fabrication of a full array tool capable of molding 50mm x 50mm PZT preforms, each having 361 fibers.

While the full array tool was being fabricated, the demonstration tool was used to prepare partial array preforms for use in binder removal and sintering process refinement. After a relatively short period of operation (less than 1000 shots) the mold inserts were disassembled and found to have excessive wear at specific points on the sliding surfaces. The wear pattern showed that abrasion from the PZT/wax mixture was not responsible for the damage. Instead the wear resulted from design features which were incorporated to ease disassembly of the ejector mechanism for cleaning and from tool materials having insufficient hardness. This information was fed back to the tool maker and new options for design were made available by MSI. Several attempts to surface harden the tool inserts, including titanium nitride coating, proved unsuccessful. In the full array tool, this problem was resolved by using an extremely hard grade of steel for the redesigned inserts.

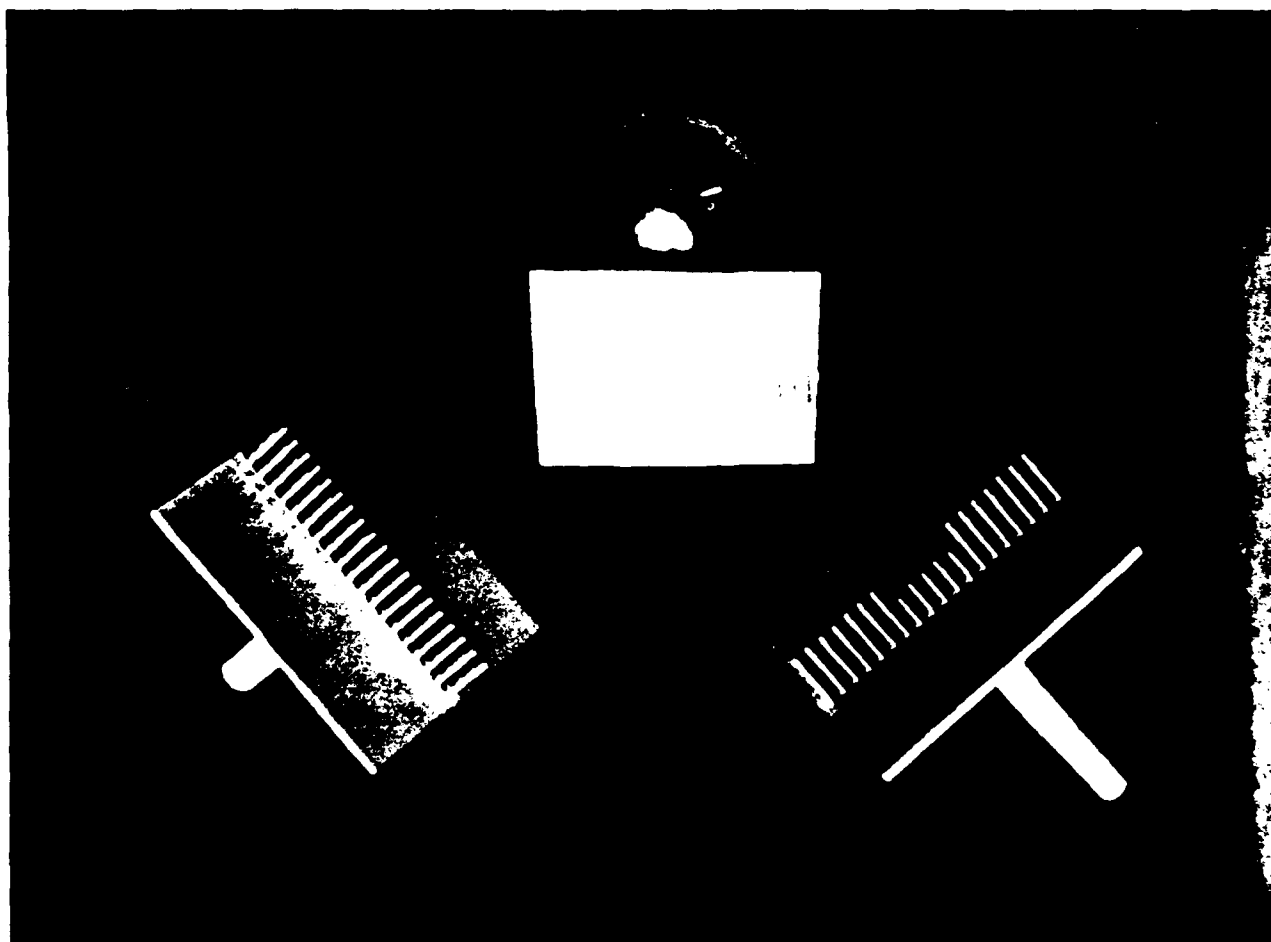


Figure 10: Molded parts made using 0.5mm diameter inserts.

The full array tool was received in mid-November 1992 after a brief delay caused by difficulties with machining the new steel, and was put into operation immediately. Figures 11 and 12 show parts made using the full array preform tool. The tool functioned well in terms of part molding, but the ejection mechanism proved insufficient to allow part removal without damage. This was resolved by incorporating an additional stage of ejection, so that the parts could be removed without the need to pull on the molded sprue. A multistage hydraulic ejector, operated independently from the molding machine hydraulics, has been designed to improve ejector operation. However, to complete the program on schedule and within budget, the mold has been used as-is to form full array PZT 1-3 preforms for deliverable composite fabrication.

Removing the sprue after molding has proved to be more difficult than expected. Complete sprue removal is important for successful binder burn-out without cracking. The molded material is abrasive and resistant to cutting. A special fixture for holding the part during sprue removal has been designed, built and tested with limited success. At present the sprue is removed while the part is still warm from molding so that stress on the part is minimized. Ultimately, the best solution is to design and build a hot sprue into the mold so that no sprue waste is formed during molding. This approach has the added advantage of improving materials utilization efficiency and thereby reducing manufacturing cost.

Approximately 200 parts suitable for burnout were produced for use in sintering studies and deliverables fabrication. With the current tool design and suitable control of the molding step, the process has shown potential for achieving very high yields of defect-free molded parts.

### *Binder Removal*

The binder removal mechanism is complex, requiring hold points in the temperature-time profile to allow for wicking out the melted wax and for controlled pyrolysis and oxidation. Furthermore, the binder removal process must be adjusted in conjunction with changes in the powder processing, compounding and molding parameters to realize a successful overall forming method.

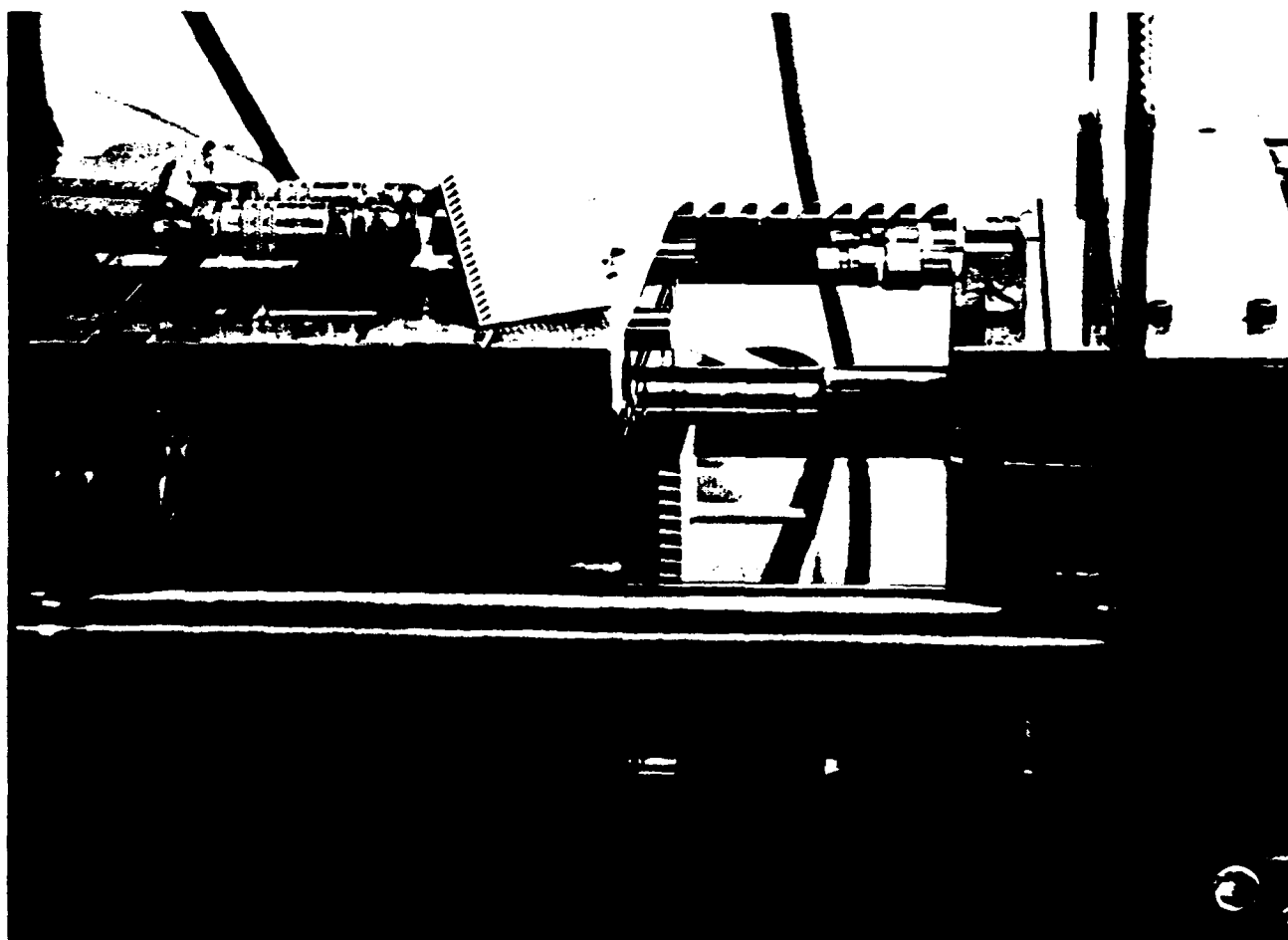


Figure 11: MSI injection molding tool showing molded parts.

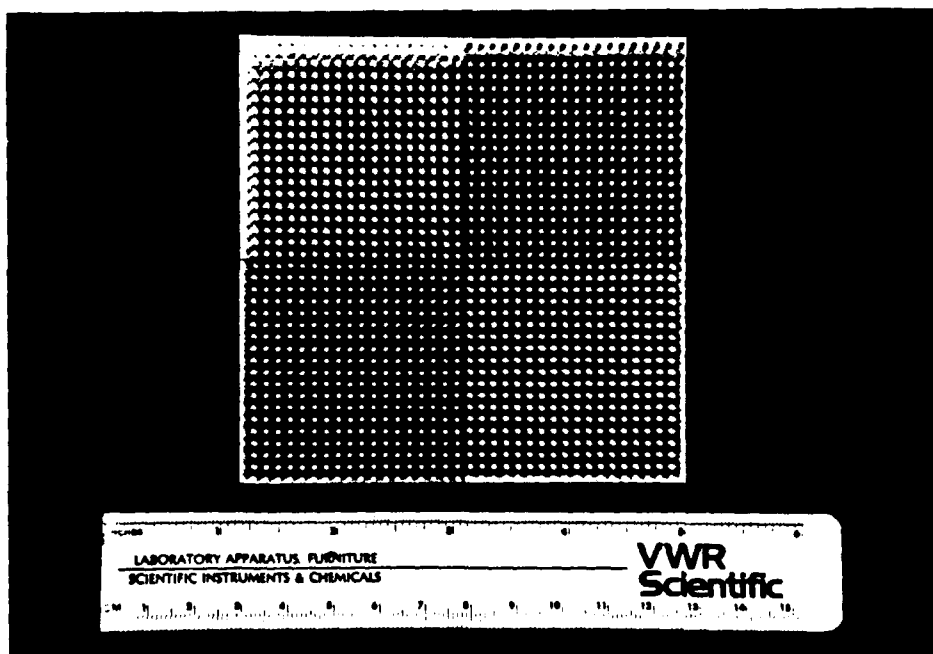
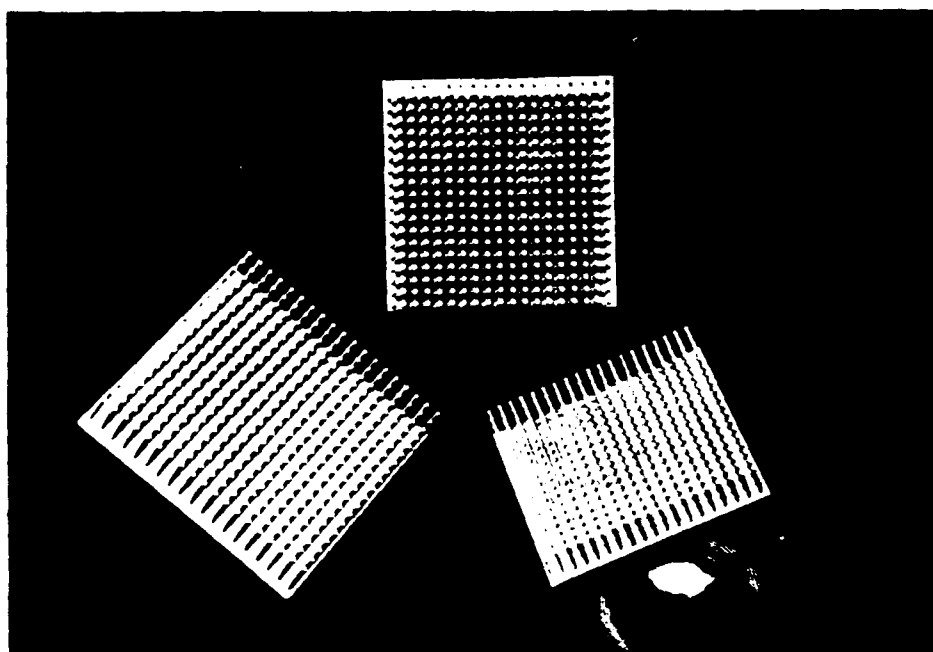


Figure 12: Injection molded and sintered full array preforms.

To adapt the process for PZT, binder burn-out studies were performed on as-molded test bars which were available early in the program. Initial burn-out conditions were selected by extrapolation from prior experience, concentrating on experimental procedures applicable to molded fiber arrays. Several successful binder removal runs were completed, providing specimens for sintering studies, but questions remained that were specific to PZT processing. In particular, some runs generated specimens which had a mottled red or orange coloration, presumably due to local red lead oxide accumulation. This observation was reviewed with the PZT powder manufacturer and found to also be common in pressed PZT parts of the same formulation. The discoloration disappeared on sintering as the lead oxide melted and dispersed throughout the parts, and had no observable impact on material properties.

The emphasis shifted onto demonstration fiber preforms as soon as these became available. An experimental review of the binder removal process was completed with the objective of establishing and controlling those parameters which most impacted part integrity. Important process variables were found to include: Binder content, support during binder remelting, air flow rate, oven loading, and sprue removal procedure.

The initial binder removal cycle was 54 hours long, compared with less than 24 hours for the sintering cycle, and thus burnout was found to be the process step limiting overall throughput. To accelerate the burnout schedule to less than 24 hours and improve the process ruggedness against cracking during wax egress from the part, the PZT/binder ratio was varied up to the maximum allowable level (limited by wear of the compounding and molding equipment), so as to minimize shrinkage during dewaxing. Initial experiments with accelerated burnout showed that a 36 hour cycle was feasible, but for very short binder removal cycles the rapid heating rate led to an increased incidence of cracking in the PZT base plate. Consequently, a second, larger burnout oven was purchased to maintain the overall production capacity using the slower 36 hour cycle.

Based on these results, the PZT powder/binder ratio was finalized, and a dimensional correction factor established for use by the tool manufacturer in building the full array tool.

The full array PZT preforms proved to be fragile after burn-out, leading to yield reduction from handling during transfer to the sintering crucibles. Since the burnout fixturing could not be adapted to survive the high temperature sintering process, experiments were conducted to establish an intermediate prefiring step at lower temperature to impart greater strength to the parts. In the current process the parts are transferred from burnout, without removal from their fixturing, into the prefiring furnace. The parts are subsequently transferred to high temperature fixturing for sintering in a separate furnace. For production, the burnout and prefire operations could be combined in the larger burnout oven to eliminate one process step.

### *Sintering*

The sintering process for injection molded PZT is similar to that for material formed via conventional processes. It is important to control the PZT chemistry and microstructure to obtain optimal properties; this is accomplished by carefully adjusting soak time and temperature, heating and cooling rates and the sintering atmosphere. In particular, the lead oxide vapor pressure is key to successful densification and grain growth since PbO is volatile at the sintering temperature.

The sintering process for 1-3 composite preforms was established using a PbO source system supplied by the PZT powder vendor. Initial sintering runs were conducted in alumina crucibles large enough for firing two PZT 1-3 preforms simultaneously. Care was taken to ensure that the crucibles fitted without gaps so that the sintering process atmosphere was reproducible. Preliminary results on PZT bars indicated that the injection molded PZT sintered readily, with no sign of any discoloration that would suggest metallic contamination from the molding process.

Sintering parameters for the 1-3 ceramic preforms were examined in detail in an effort to optimize the piezoelectric properties of the injection molded PZT. For this purpose, coupons of injection molded PZT from the preform base were sintered in closed high purity alumina crucibles in tiered stacks. The heating and cooling rates were chosen to allow for the use of larger crucibles, in anticipation of future scale up. Important sintering process variables were identified as follows: The combination of heat/cool rate, soak temperature and time; PbO source location

and quantity; and crucible loading. No problems were encountered with sintering warpage, provided the preform base was uniformly supported during sintering.

Figure 13 shows the piezoelectric properties (measured at MRL, Penn State Univ.) of the injection molded PZT coupons. These data are plotted as a function of weight change during sintering. (Weight change is a convenient parameter for normalizing the data from various sintering runs because it reflects changes in the system chemistry; however, other important dependent variables include density and microstructure.) It can be seen that the range of acceptable sintering conditions is narrow, but that the optimum conditions yield properties which are almost identical to those specified by the powder manufacturer (see Table 2).

Having scoped out an acceptable range of sintering parameters, the main technical emphasis was placed on reproducibility and fixturing development for subsequent scale up. Sintering experiments were conducted on molded PZT test coupons and test configuration preforms with the objective of refining the sintering conditions and establishing fixturing needs. Approximately thirty PZT test coupons were fired as part of a controlled experiment to determine the reproducibility of the electrical properties around the peak values in Figure 13. Measurements at MRL, Penn State, showed  $d_{33}$  values ranging between 680 and 750 pC/N, and relative permittivities from 3300 to 3500. Values within these ranges were obtained over a wide range of sintering temperature/time profiles provided provisions were made to properly control the sintering atmosphere and part location with respect to the PbO source. A set of standard sintering conditions for this PZT-5H powder lot was then established for use in deliverables fabrication. In addition, sintering fixturing configurations and materials were identified that allowed fired preforms to remain acceptably flat after densification. New larger crucibles were purchased capable of firing 12 to 18 full array preforms per crucible.

Using the production-sized crucibles, a production simulation run of 50mm x 50mm injection-molded PZT-5H preforms was made during February 1993. A total of thirty-eight (38) preforms were sintered, either 2 or 4 parts per run. The parts were fired under standard conditions in a closed alumina crucible containing a predetermined amount of PbO-containing source powder to control the weight change during densification. The weight change was measured for all parts in the



**Table 2: Properties of Injection Molded and Pressed PZT-5H Ceramics.**

<b>MATERIAL</b>	<b>DENSITY (g/cc)</b>	<b>RELATIVE PERMITTIVITY</b>	<b>DIELECTRIC LOSS (1kHz)</b>	<b>d<sub>33</sub> (pC/N)</b>
<b>Die Pressed*</b>	<b>7.51</b>	<b>3584</b>	<b>0.018</b>	<b>745</b>
<b>Injection** Molded</b>	<b>7.55</b>	<b>3588</b>	<b>0.018</b>	<b>755</b>

**All electrical properties measured 24 hours after poling.**

**\* Manufacturer's data measured on the same powder lot.**

**\*\* Properties measured by MRL, Penn. State.**

production run as the primary process control variable. Physical dimensions and immersion densities were also measured on a spot-check basis.

Weight-loss, dimension, and density data were very reproducible with the standard deviation of the weight loss being 0.05% (see Figure 13). Fired density was consistently 7.51( $\pm$ 0.02) g/cc. The dimensions of the fired parts were:

Base plate	49.15 x 49.15 ( $\pm$ 0.05) mm
Fiber length	7.9 mm
Fiber mid-point diameter	1.1 mm
Fiber spacing (center-to-center)	2.59 mm
Fibers per preform	361
PZT volume fraction	15%

## 4.2 Composite Fabrication

### *1-3 Composite Fabrication Studies*

Composite fabrication studies were conducted using 50x50 mm sintered PZT-5H preforms and several polymer matrix materials. The objective of the studies was to gain experience with various materials and potential manufacturing processes prior to fabricating the the 100x100 mm deliverables and eventually 0.5x0.5 meter panels for the 2m x 2m manufacturing demonstration. Both rigid and flexible polymer matrix materials were studied. (Flexible polymers will be used in the future for the 2m x 2m array.) However, rigid epoxy was used for the deliverable composites in the present program, so that the samples could be directly compared with Spurr epoxy composites tested by ONR in other work.

The specific polymer matrix materials investigated in this program were:

#### Rigid:

Spurr epoxy (standard formulation)  
Polyester resin + methyl ethyl ketone peroxide hardener

#### Flexible:

Conap EN-2 polyurethane  
Voided Conap EN-2 (w/ 40% Expancel 551DE microspheres)

The experimental approach was to place a single preform in a 50 mm square rubber mold and to pour liquid polymer into the mold to immerse the preform (Figure 14). After the appropriate cure cycle, the mold was peeled away from the composite. The preform base plate was then machined away or, in some cases for flexible polymer matrices, the composite could actually be peeled away from the base plate. Once the base plate was removed, both sides were ground flat and the composite evaluated.

A characteristic of the rigid Spurr epoxy material was volume shrinkage during cure. This caused the polymer-ceramic portion of the body to contract against the all-ceramic base plate. The differential contraction created stresses which caused warping, and in some cases, cracking of the epoxy matrix. This phenomenon did not occur with the flexible polymers.

For the flexible polymer matrix samples, it was observed that, even though no adhesion aids were used in preparing the ceramic preforms for encapsulation, the polymer bonded to the individual fibers, but the bond was weaker than in the case of the rigid polymers. (In many cases, it was possible to push out the fibers with moderate force; this reduced bond strength may actually result in improved acoustic performance in end-capped transducers.) One 100mm square and several 50mm square solid polyurethane matrix composites were prepared and poled by both the contact method and corona poling. The as-encapsulated composites showed sufficient bond integrity for poling provided they were not substantially flexed beforehand. Composites that were highly flexed prior to poling exhibited sporadic dielectric breakdown at the highest field levels, presumably due to the creation of an air gap along the length of a few of the fibers during flexing.

Voided EN-2 polyurethane proved more difficult to formulate and encapsulate because the time required for homogeneously mixing the microvoids with both parts of the polymer was close to the pot life of the mix. Although the mixture was quite viscous, it proved possible to fill the space between the fibers satisfactorily using the open-mold process. Use of a similar polymer with longer working life would simplify and improve the process.

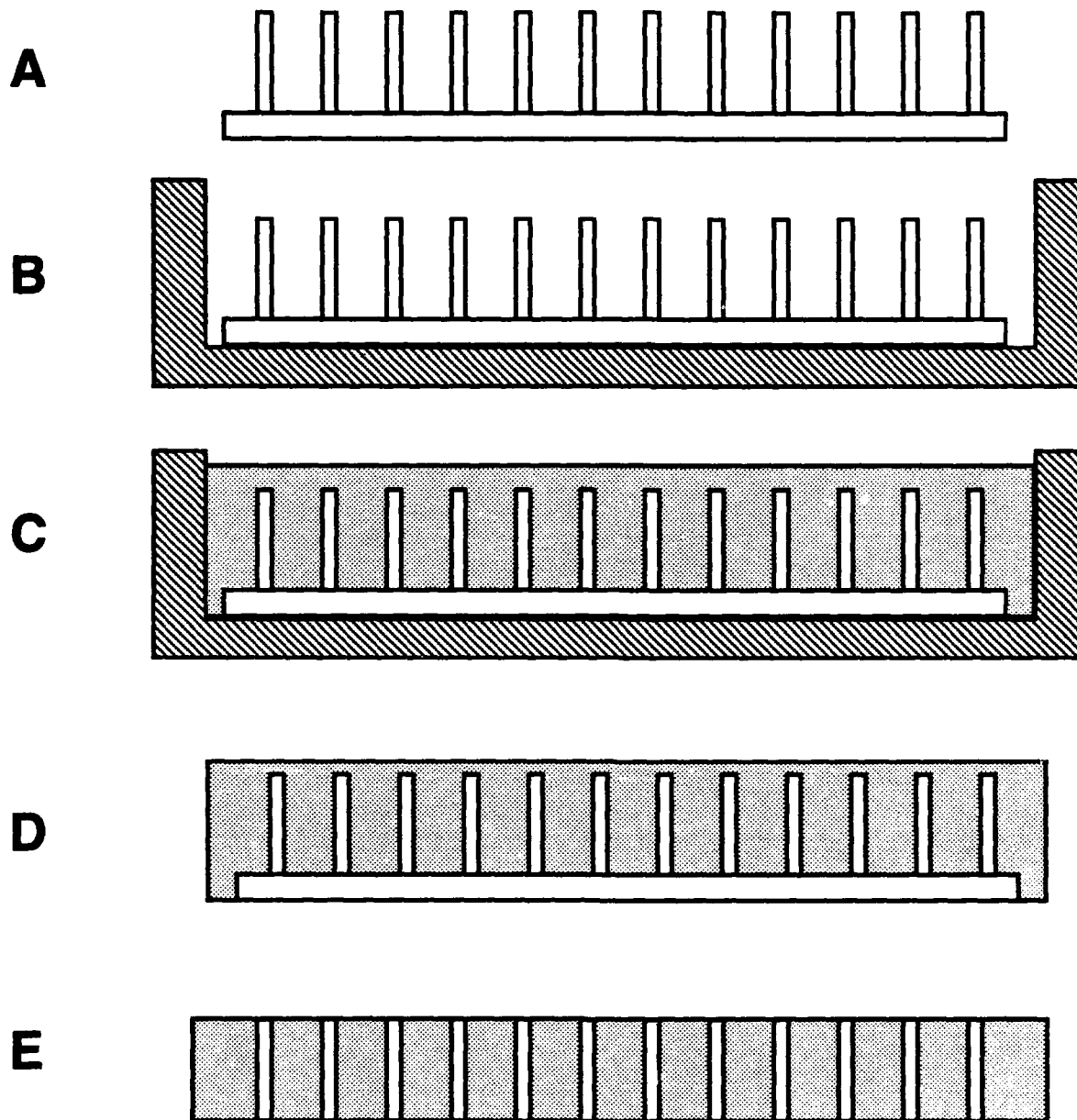


Figure 14: Schematic description of 1-3 composite fabrication process.  
 (A) Injection molded ceramic preform. (B) Preform in rubber mold.  
 (C) Liquid polymer poured into mold. (D) Composite removed from  
 mold after curing. (E) Composite after machining of both faces.

A total of four 50mm square composite samples were made using 40 volume percent voided polyurethane as the matrix material. Techniques to produce composites having PZT fibers extending beyond the matrix (Figure 15) were also investigated. (This configuration has been proposed by Vector Research as an enhanced acoustic performance composite.) With this configuration, face plate attachment was accomplished readily via adhesive bonding directly to the exposed fibers. A method was demonstrated for extending the fibers above the matrix surface on either one or both sides of the composite. As a demonstration, glass reinforced plastic face plates were bonded to both ends of the fibers in two separate 50x50 mm composites samples (Figure 16).

#### *Fabrication of 100x100 mm 1-3 Composite Deliverables*

Composite Fabrication. Four sets of 4 PZT sintered preforms each were incorporated into deliverable 100x100 mm 1-3 composites. The 4 preforms were arranged in a 114 mm square rubber mold and covered with approximately 150 ml of Spurr epoxy, (Polysciences, Inc., Warrington, PA). The standard ("firm") formulation of Spurr epoxy was used for all the deliverable composites.

To minimize warping, a cure schedule for the Spurr epoxy was developed that allowed curing over a period of several days to minimize differential shrinkage. After 4 days at 30°C, the epoxy became solid but flexible, allowing the PZT preform base plates to be ground away with conventional fixed abrasive tooling. Once the base plates were removed, the epoxy composite was heated to 70°C for several hours to complete the cure. It was found that even after full curing, the epoxy material was somewhat rubbery when reheated to 70°C. This effect was used to relieve any residual stresses prior to final machining.

Final machining was accomplished with conventional fixed abrasive grinding wheels to make both sides flat and parallel and to achieve a thickness of approximately 6.35 mm. Several of the deliverable composite samples are shown in Figure 17.

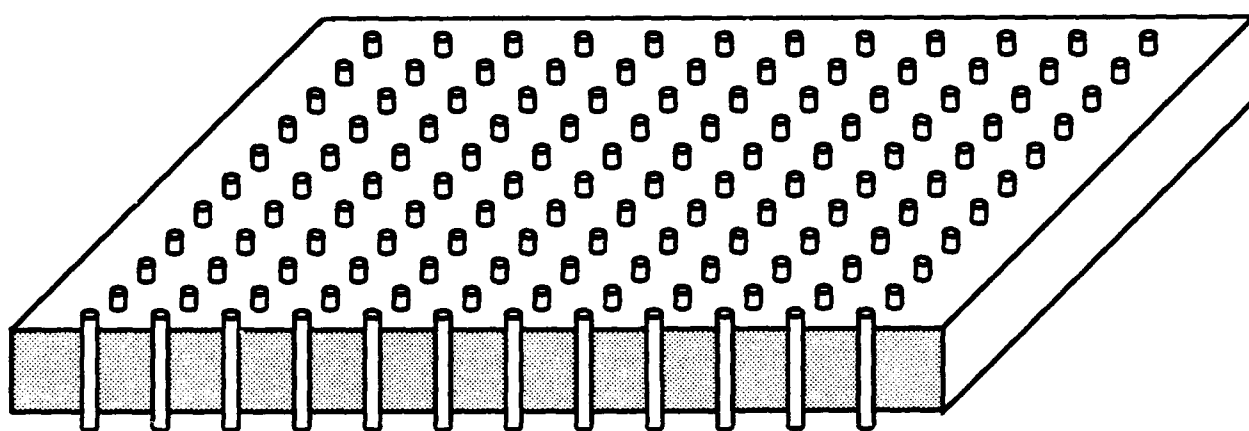


Figure 15: Schematic of composite with extended fibers.

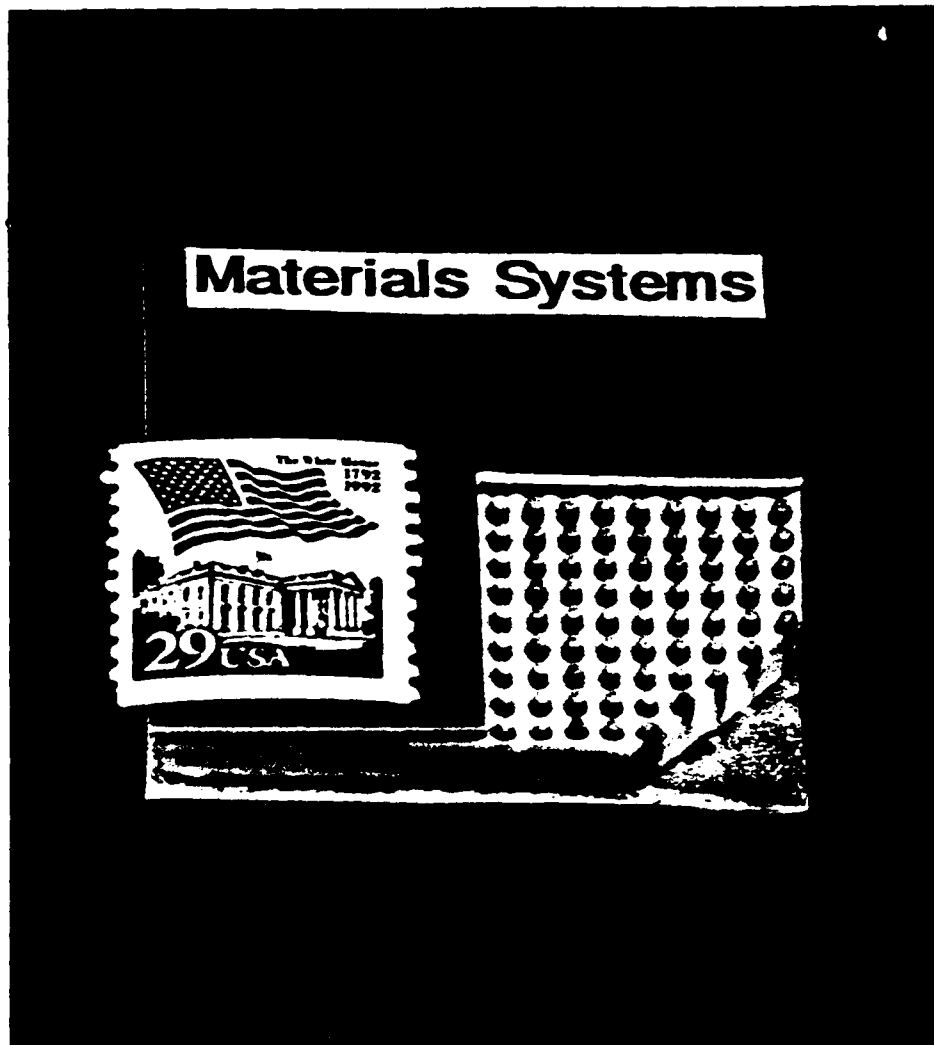


Figure 16: Prototype 1-3 composite with glass-reinforced plastic face plates and voided polyurethane matrix. This composite also features 15 volume percent injection molded PZT fibers and 0.5 mm air gaps on both sides.

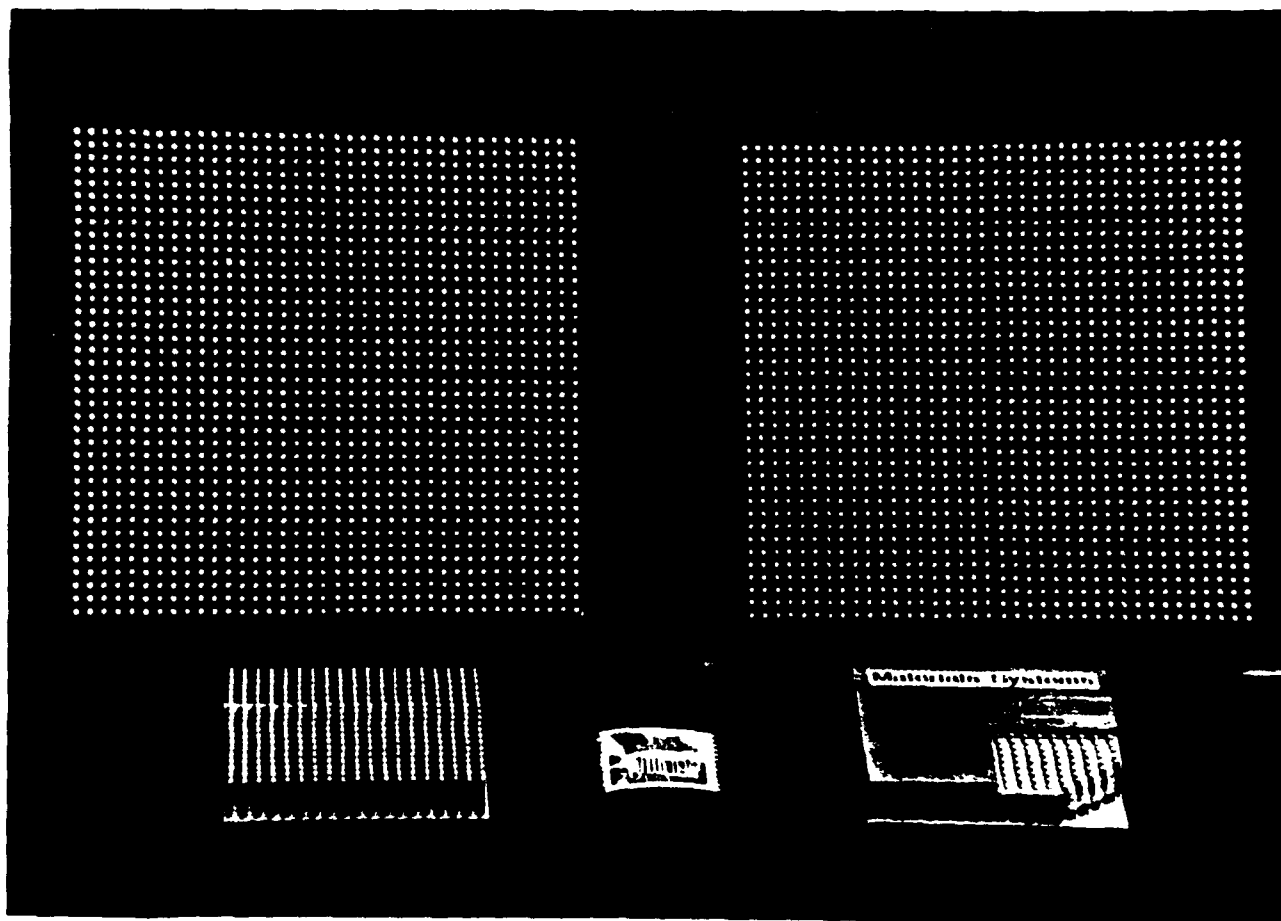


Figure 17: Composite deliverables.

Poling. Two of the four 100x100 mm composites were contact poled by Dr. Thomas Shrout at Penn State University. Silver paint electrodes were applied to both sides and then the samples were subjected to a field of 23 kV/cm for 15 minutes at room temperature. Normally, contact poling must be done in an oil bath to prevent shorting around the sample edges. However, the approximately 8 mm wide all-epoxy border on the 100x100 mm composites permitted the samples to be poled in air. Saturation polarization occurred rapidly as soon as the field levels were raised to the maximum, as evidenced by changes in  $d_{33}$ , relative permittivity, and dielectric loss.

The remaining two 100x100 mm composites were corona poled by Prof. Ahmad Safari at Rutgers University. No electrodes were required for corona poling. The poling conditions were: 70 C, 30 minutes and 24kV tip-to-ground voltage.

During poling of the deliverable samples, which contained a total of 5776 fibers, dielectric breakdown occurred at 4 points. The breakdowns were found to have occurred along the fiber-epoxy interface, rather than through the fiber itself, and appeared to be associated with voids or other defects in the epoxy. Because the breakdown created a conductive carbon path through the thickness of the sample, at the suggestion of Vector Research the breakdown points were filled with room temperature epoxy in order to avoid spurious electrical interference during subsequent testing.

These poling results emphasize the desirability of poling the PZT preforms prior to encapsulating in the matrix. By this means the poling process would be completed before significant value is added to the composite and without concern regarding dielectric breakdown due to the polymer interface or matrix integrity. Overall process yield would be favorably impacted for reduced composite cost. This option is available with injection molded preforms.

### Measurements.

The poled composites were first characterized for capacitance and dielectric loss changes before and after poling as an indication of the extent of poling in the PZT fibers. For most samples the dielectric constant increased by 70% during poling while the dielectric loss decreased approximately 10%. These changes were typical for injection molded ceramic PZT-5H and indicated that poling had reached saturation.

Piezoelectric properties are difficult to measure in 1-3 composites unless a hydrostatic method is used. For the purposes of developing a method for routine characterization, the  $d_{33}$  meter was used at both Penn State and Rutgers Universities and FMI. Measurements were made with point contacts placed directly on the fibers and on the matrix in between fibers to give an indication of degree of fiber-matrix mechanical coupling. All measurements were made at least 24 hours after poling to ensure that aging effects were minimized, and painted silver electrodes were applied so that all of the available response was detected by the  $d_{33}$  meter.

Table 3 summarizes the  $d_{33}$  data from measurements on the various MSI 1-3 composite samples. As-expected, the  $d_{33}$  values measured on embedded fibers are less than those of the equivalent ceramic because of the mechanical restraining effects of the polymer. There appears to be no consistent difference between samples which are corona or contact poled, either method is capable of effectively poling the material. In general, the samples made with flexible matrices poled more rapidly than those made with rigid epoxy, as expected from polymer restraint considerations. Variations in the  $d_{33}$  values between 100mm square samples made with Spurr epoxy are difficult to explain. Each sample contains four 50mm PZT preforms selected at random from several of the controlled sintering production runs, and therefore the PZT is unlikely to have caused variations in the composite properties. It is possible that there are variations in the properties of the Spurr epoxy matrix due to the complex cure schedule. However, measurements of the hardness of the Spurr epoxy matrix made using the Balcor technique at U. Mass. Lowell showed no detectable differences among the four deliverable specimens. More likely, the measurement technique itself is subject to variations since both Rutgers and Penn State had difficulty handling the large 100mm square composites in the instrument during  $d_{33}$  measurement.

Overall, the composite properties appear good based on the limited data available at this time. We recommend that a thorough evaluation of the properties be performed by ONR on the deliverable specimens, emphasizing reproducibility from piece to piece so that the data can be used to guide further process development.

**Table 3: Properties of Injection Molded PZT-5H 1-3 Composites.**

<b>DATA SOURCE</b>	<b>SAMPLE TYPE</b>	<b>d<sub>33</sub> (pC/N)</b>	<b>COMMENTS</b>
<b>MRL, Penn. State*</b>	<b>2" Spurrs epoxy</b>	<b>530</b>	<b>On fibers</b>
	<b>2" Spurrs epoxy</b>	<b>280</b>	<b>Between fibers</b>
	<b>4" Spurrs epoxy</b>	<b>420</b>	<b>On fibers</b>
	<b>4" Spurrs epoxy</b>	<b>330</b>	<b>Between fibers</b>
<b>MRL, Penn. State*</b>	<b>2" solid soft polyurethane</b>	<b>520</b>	<b>On fibers</b>
		<b>235</b>	<b>Between fibers</b>
<b>Rutgers Univ.**</b>	<b>4" Spurrs epoxy</b>	<b>600</b>	<b>On-fibers</b>
	<b>4" Spurrs epoxy</b>	<b>450</b>	<b>On-fibers</b>
<b>FMI**</b>	<b>2"x 4" porous polyurethane</b>	<b>458</b>	<b>FMI encapsulation, MSI PZT fibers</b>

\* Contact poled, aged 24h, point probes.

\*\* Corona poled, aged 24-48h, point probes.

## **5. Conclusions**

An injection molding process suitable for mass-production of 1-3 piezoelectric ceramic/polymer composites has been developed and successfully demonstrated by actual composite fabrication. The injection molded composites have good piezoelectric properties and offer flexibility in terms of composite assembly and matrix materials selection. Above all, the process has excellent potential for cost reduction and large area array fabrication. Key demonstrated features of the process include:

- High yield and cost effective.
- Rugged against process variations.
- Versatile in terms of PZT element shape, spacing, aspect ratio.
- Produces high quality material having good properties.
- Readily scaleable, high process throughput in manufacturing.
- Process addresses composite transducer manufacturing needs for both Navy and commercial ultrasonic imaging applications.

A pilot-scale manufacturing facility is established and operational for the fabrication of prototype and manufacturing quantities of 1-3 piezoelectric ceramic/polymer composites for Navy applications.

## 6. Appendix

### Presentations/Publications/Patents

1. 4/22/92: ONR Program Review, Penn State University.
2. 8/31/92: Presentation and publication at IEEE International Symposium on Applications of Ferroelectrics, Clemson University, South Carolina.
3. 4/6/93: ONR Program Review, Penn State University.
4. 4/21/93: Presentation at the American Ceramic Society Annual Meeting, Cincinnati, Ohio.
5. 4/5/93: Patent application: Method for Making Piezoelectric Ceramic/Polymer Composite Transducers.